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(54) **Improvements in or relating to the preparation of fibre-reinforced composites**

(57) A fibrous reinforcement assembly with a mixture of a liquid resin and a curing agent for the resin. The fibrous reinforcement assembly further comprises a physiochemical immobilisation means (110) disposed

at one or more locations on and/or within the fibrous reinforcement. The immobilisation means is configured to impart the localised immobilisation of the liquid resin in the vicinity of the immobilisation means.

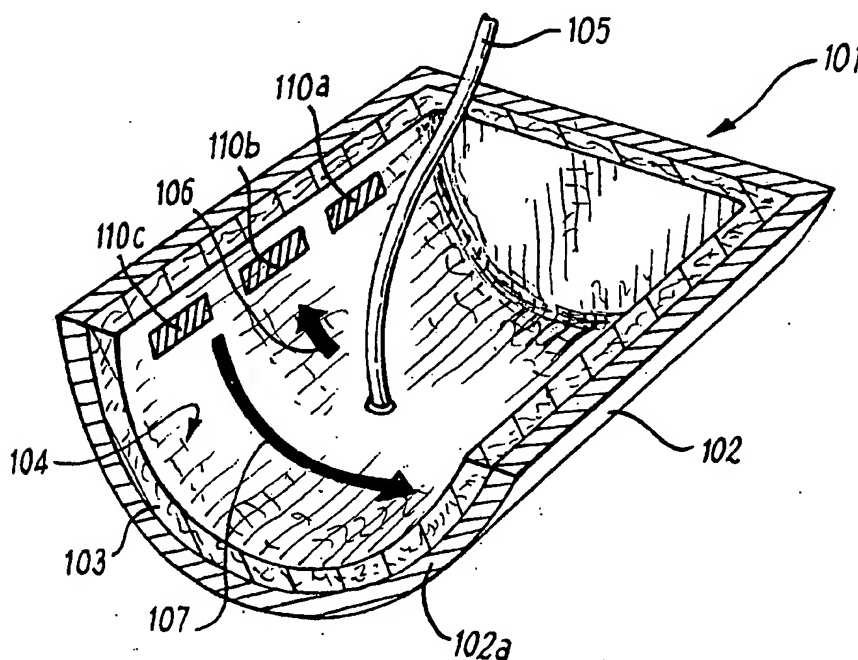


FIG. 1

Description

[0001] The present invention relates to improvements in or relating to the preparation of fibre-reinforced composites.

[0002] Fibre-reinforced composites are widely used to form structures and components for use in a range of different industries including, for example, the aerospace, transport, electronics, building and leisure industries.

[0003] A common approach for the preparation of such structures or components, especially large structures or components such as boat hulls, wind turbine blades, or certain aircraft components, involves the arrangement of a fibrous reinforcement assembly within a mould followed by the impregnation or infusion of the assembly with a mixture of one or more liquid resins with one or more curing agents. Once the impregnation or infusion of the liquid resin/curing agent mixture into the assembly is complete, the liquid resin is then cured to yield the final moulded structure or component, typically by heating the assembly.

[0004] There are a number of different techniques by which a resin/curing agent mixture may be infused or impregnated into the fibrous reinforcement assembly. Conventional techniques involve either brushing or metering the resin/curing agent mixture onto the fibrous reinforcement. Although such techniques are simple and relatively inexpensive to implement in practice, the resultant product can be variable in quality and the mechanical properties of the final structure or component can often be poor.

[0005] More recently, liquid resin infusion technologies, known in the art by various acronyms such as RTM, VaRTM, SCRIMP, RIFT etc., have been developed. All of these technologies rely on the basic concept of injecting or infusing the resin into the fibrous reinforcement assembly, either in a closed mould in the case of an RTM process, or in a vacuum bag moulding in the case of a VaRTM or a SCRIMP process. These processes carry numerous advantages over the conventional techniques by virtue of the improved hygiene and safety with which these mainly enclosed processes can be carried out, the favourable mechanical properties of the final composite component or structure, and favourable manufacture costs.

[0006] When preparing fibre-reinforced components by a liquid resin infusion process, it has been observed that there is a tendency for the liquid resin infused into the fibrous reinforcement assembly to become depleted within certain areas of the assembly during infusion and cure. This occurrence is especially common when a vacuum resin infusion process is used to prepare large components, such as a wind turbine blade or boat hull, for example, and/or when the liquid resin infused into the fibrous reinforcement assembly is of particularly low viscosity (low viscosities giving particular benefits in infusion speed, for example). The occurrence of resin de-

pletion can be particularly disadvantageous because the final structure or component formed following the cure of the liquid resin does not contain the originally intended distribution of resin throughout its structure. As a consequence, the mechanical properties and performance of the structure or component thus formed can be compromised, particularly in the regions where resin depletion has occurred. The occurrence of resin depletion can often be visualised by the presence of white patches on the surface of glass reinforced components. These may appear during infusion or may only become apparent following curing.

[0007] In the case of a VaRTM process, for example, the areas of the assembly that have been observed to be particularly prone to the occurrence of resin depletion include the areas in the vicinity of the suction tubing that connects the vacuum pump to the mould, where resin depletion tends to occur as a result of the suction force generated by the vacuum pump, and areas that are in contact with vertically inclined sections of the mould, where resin depletion can also result from the effect of gravity. Resin depletion in these areas is especially likely to occur once all the interstices between fibres of the fibrous reinforcement have become fully saturated with the infused liquid resin. Furthermore, the support pressure applied to the assembly by the vacuum bag is typically less than 1 bar (100kPa), which in itself is insufficient to prevent the liquid resin flowing out of the vertically inclined sections of the composition under the force of gravity.

[0008] If the resin is an epoxy resin, the problem is further exacerbated when the assembly is heated to cause the resin to cure because the viscosity of the epoxy resins can decrease significantly during the cure cycle. Although common to other resin systems, liquid epoxy resins are less likely to be able to counteract this viscosity decrease by a rapid gelation and cure mechanism. This temporarily unchecked reduction in viscosity, particularly when coupled with the fact that it is often necessary to maintain the vacuum suction to the assembly once the resin infusion is complete and also during the cure cycle, further increases the tendency for the resin depletion to occur, particularly in susceptible areas.

[0009] One approach to solve this problem is to use a very rapid curing system; the gel time for formulated epoxy resin infusion systems can be reduced to just a few minutes or, in some cases, even less. However, this can impact severely on the viscosity of the composition during the infusion process, and the safety of the operation, such high reactivity often being accompanied by high exothermic heat generation.

[0010] It is an object of the present invention, therefore, to provide a process and composition for the preparation of a fibre-reinforced composite structure or component by a resin infusion process in which depletion of resin in areas that are prone to resin depletion is significantly decreased or eliminated altogether.

[0011] According to a first aspect of the present invention there is provided a fibrous reinforcement assembly impregnated with a mixture of a liquid resin and a curing agent for the resin, wherein said fibrous reinforcement assembly further comprises immobilisation means disposed at one or more locations on and/or within the fibrous reinforcement, said immobilisation means being configured to impart the localised immobilisation of the liquid resin in the vicinity of the immobilisation means.

[0012] Preferably, the immobilisation means is a physicochemical means by which the viscosity of the liquid resin may be increased. The physicochemical immobilisation means may comprise the addition of an additive with an intrinsic viscosity-enhancing property, such as a thickening or thixotropic agent, or, alternatively, the addition of an accelerator agent that reacts with the liquid resin/curing agent mixture to form a gel. The increase in viscosity imparted in the liquid resin can be exploited to either immobilise a region of the liquid resin within the assembly or to create a barrier to prevent, or at least impede, the flow of liquid resin from a specified area of the assembly.

[0013] Alternatively, the immobilisation means may be a physical barrier which is positioned within the assembly to prevent or at least impede the flow of resin from a specified area of the assembly.

[0014] According to a second aspect of the present invention there is provided a process for the preparation of a fibre-reinforced composite structure or component comprising the steps of:

(i) placing a fibrous reinforcement assembly in a mould for said structure or component;

(ii) infusing said fibrous reinforcement assembly with a mixture of a liquid resin and a curing agent for said liquid resin; and

(iii) facilitating the cure of said liquid resin;

wherein immobilisation means is disposed at one or more locations on and/or within the fibrous reinforcement, said immobilisation means being configured to impart the localised immobilisation of the liquid resin in the vicinity of the immobilisation means.

[0015] The problem of resin depletion observed to occur following the preparation of a fibre-reinforced composite structure or component by a resin infusion process can be solved by the present invention by the selective positioning of the immobilisation means in the areas of the assembly that are prone to resin depletion (i.e. vertically inclined sections of the mould or, in a VaRTM process for example, the areas surrounding the vacuum tubing), thereby enabling the formation of a final cured structure or component having a substantially uniform distribution of resin throughout its structure. It will be appreciated that the localised immobilisation of the liquid resin in the vicinity of the immobilisation means

prevents, or at least substantially reduces, the tendency for resin to flow out of these areas, whether under the force of gravity or by any other driving force.

[0016] In addition to providing a solution to the problem of resin depletion, there may also be instances where the controllable localised immobilisation of the resin may be used to achieve other desired effects, such as, for example, to close off or block a suction tube connection between the vacuum pump and the mould assembly in either a VaRTM or a SCRIMP process. This effect could be desirable to facilitate the controlled infusion of the resin into the assembly and could be achieved by the placement of an immobilisation means in the vicinity of the opening of a vacuum suction tube so that once the resin reaches the immobilisation means and the localised immobilisation of the infused resin is imparted, then that suction tube will become effectively closed off or blocked. This effect could be exploited to sequentially close a number of different suction tubes as the liquid resin gradually infuses into different regions of the assembly, thereby enabling the vacuum suction to become gradually more concentrated in the remaining areas of the assembly where complete infusion has not been achieved.

[0017] Known methods by which the localised immobilisation of a liquid resin within the assembly could be achieved by the direction of heat to localised areas of a prepreg composition, thereby promoting the cure of the resin in that locality, are described in Butler *et al.*, Proc. Int. Conf. Compos. Mater., 10th (1995), Volume 3, 269-276 and Shull *et al.*, Proceedings of SPIE - The International Society for Optical Engineering, (2000), 3993, 19-22. In such processes, however, the possibility exists for thermal transfer to promote the cure of resin beyond the localised areas desired. Where the resin system is formulated to be highly reactive, i.e. when a rapid cure at low temperatures is desired, for example, then the possibility exists for promotion of the cure reaction via exothermic enhancement. Unless measures are taken to limit this, there is the potential for the cure of the resin to be promoted throughout larger areas of the composition, particularly in thick sections of the assembly. In contrast, some of the compositions and processes of the invention described herein, do not rely on vigorous reaction chemistry to achieve localised immobilisation of resin, thus removing the problem of unwanted exothermic enhancement.

[0018] In the present invention the expression 'immobilisation means' is used herein to denote a means of imparting the localised immobilisation of the liquid resin infused into the fibrous reinforcement assembly by either a physicochemical means by which the viscosity of the liquid resin may be increased or the provision of a physical barrier on or within the assembly to prevent or impede resin flowing out of a selected region of the assembly.

[0019] It is especially preferred that the immobilisation means is a chemical means by which the viscosity of

the liquid resin is increased by the reaction of a so-called 'accelerator agent' with the infused liquid resin/curing agent mixture. This reaction increases the viscosity by inducing the localised gelation of the liquid resin, thereby preventing the liquid resin from flowing freely in the region where the chemical means is applied and thus, can be used to prevent the occurrence of resin depletion.

[0020] The reaction of the liquid resin/curing agent mixture with the accelerator agent does not necessarily result in the full cure of the resin in the vicinity of the immobilisation means. It is merely required that the viscosity of the liquid resin is increased to a sufficient extent to prevent its flow and, hence, its depletion, from the vicinity of the chemical means. The full cure of the immobilised region can occur by the continued reaction between the resin and the curing agent, often at elevated temperature. Alternatively, the accelerator agent applied in this region may also be involved in this continued reaction.

[0021] The accelerator agent may be applied either directly onto and/or impregnated within the surface of the fibrous reinforcement assembly or, where this assembly is composed of a number of sheets or plies of a fibrous reinforcement material, the accelerator agent may be applied onto and/or impregnated within some or all of those individual sheets or plies. The latter form of application is particularly desirable when a comprehensive immobilisation of the liquid resin throughout the assembly is desired at a given location.

[0022] As the liquid resin/curing agent mixture infuses into the fibrous reinforcement assembly, the accelerator agent might become dispersed into the surrounding area. This being the case, it is anticipated that the use of the accelerator agent would be most appropriate in areas of the assembly where the rate of resin flow through the assembly is low during the infusion process. In practice, most of the areas of the assembly that are prone to resin depletion and hence, where the immobilisation of the liquid resin is desired, are located around the periphery of the assembly where the assembly is typically thinner and the rate of resin flow is typically low. Accordingly, in these areas, the dispersion and dilution of the accelerator agent into the surrounding area by the flow of the infusing resin/curing agent mixture will be limited.

[0023] Preferably, the localised reaction between the accelerator and the liquid resin/curing agent mixture occurs at a time nearing the end of the resin infusion when the flow rate is low.

[0024] In the case of a SCRIMP process, where rapid flow of the liquid resin/curing agent mixture across the surface of the lower surface of the assembly is encouraged before permeating towards the mould surface, the accelerator would preferably be applied to a number of plies throughout the thickness of the fibrous reinforcement assembly, rather than just on the surface of the assembly.

[0025] In the case of VaRTM processes, the acceler-

ator agent can be applied to the fibrous reinforcement prior to evacuating the assembly and infusing the fibrous reinforcement with the liquid resin/curing agent mixture.

[0026] Although a neat application of the accelerator agent onto the fibrous reinforcement assembly is generally preferred, some additional components may be included with the accelerator agent to assist in the immobilisation of the accelerator within and/or on the surface of the fibrous reinforcement. An example of one such additional component that may be used is a thixotropic material such as fumed silica available from Cabot Corporation under the tradename Cabosil® or from Degussa Ltd. under the tradename Aerosil®.

[0027] Where the loading of neat accelerator at any given location is likely to give a local accelerator concentration that is too high, then the accelerator can be dissolved in a solvent that can be flashed off later. It is important that any carrying solvent is removed completely and this can be done using heat and/or vacuum processes. It will be clear to a person skilled in the art that such a technique may be carried out during a vacuum resin infusion process by the evacuation of the assembly prior to resin infusion if the accelerator is supplied as a solution. Furthermore, the supply of a solution of the accelerator may facilitate application of the accelerator to the fibrous reinforcement by a suitable spraying or painting technique by the moulder. It may then be appropriate for the carrying solvent to be removed as described above, relying on the use of the vacuum normally associated with drawing the liquid resin into the assembly. However, any limitations imposed by the activity of the accelerator need to be taken into account.

[0028] It is preferred, however, that the accelerator agent is applied to the fibrous reinforcement assembly in the form of a so-called "accelerator-preg". By "accelerator-preg", we mean a patch or strip of a suitable carrier substrate which is impregnated with an accelerator agent.

[0029] The "accelerator-preg" may be supplied separately as patches or strips of carrier substrate which have been pre-impregnated with the accelerator agent. Hence, according to a further aspect of the present invention, there is provided an "accelerator-preg" suitable for placement on and/or within a fibrous reinforcement assembly comprising a carrier substrate impregnated with an accelerator agent as herein defined.

[0030] The use of an "accelerator-preg" is particularly advantageous because it obviates the requirement for the moulder to handle the accelerator agent directly. As for the application of the accelerator agent directly onto the fibrous reinforcement discussed above, it is preferred that the carrier substrate is impregnated with neat accelerator, but it may be necessary in some cases to add additional components (e.g. Cabosil®) to assist the immobilisation of the reactant either within or on the surface of the carrier substrate.

[0031] Any suitable carrier substrate may be used for the preparation of an "accelerator-preg". Suitable exam-

plies include textile materials, especially lightweight fabrics and scrims of natural or synthetic fibres such as nylon, polyester, cotton glass or carbon fibre in stitched, knitted, woven or mat form. Accordingly, the carrier substrate of the "accelerator-preg" could either be the same material as the fibrous reinforcement assembly or different. In most cases, an "accelerator-preg" will be applied to thin sections of the fibrous reinforcement. In such cases, a sufficient quantity of the accelerator can be impregnated onto a lightweight fabrics material such as, for example, the scrims or carriers often used in adhesive technology. These very lightweight impregnated articles are especially suited for inclusion in many areas of, for example, a wind turbine blade lay-up or a boat hull, because their effect on the performance of the final component is likely to be negligible. The "accelerator-preg" may be applied onto the surface of the fibrous reinforcement or, alternatively, where the fibrous reinforcement is composed of a number of plies or sheets of reinforcement material, the "accelerator-preg" may be applied in between some or all of those plies or sheets. The latter form of application is particularly desirable when a comprehensive immobilisation of the resin throughout the entire thickness of the fibrous reinforcement assembly is required. In some cases, it may be preferable to stagger the "accelerator-pregs" applied between the respective sheets or plies of the fibrous reinforcement so that a gradual and controlled increase in the viscosity of the resin is imparted as the resin infuses through the assembly. This is especially desirable in thick sections of the assembly, where the resin flow is likely to be high.

[0032] The accelerator agent could be applied to the carrier substrate of the "accelerator-preg" in a solvent, as described above in relation to the application of the accelerator directly to the fibrous reinforcement assembly. In such cases, the solvent impregnation and subsequent solvent removal could form part of the "accelerator-preg" manufacturing process.

[0033] The carrier substrate may be secured to the fibrous reinforcement assembly using a small stitch or knot of glass fibre, in a similar manner to the way in which the various plies of the fibrous reinforcement assembly are typically secured to each other. Experimentation will determine the optimal positioning for these patches for each application, both in the x-y plane (in the plane of the reinforcement) and in the z plane (through the assembly). The precise positioning is likely to be unique for each lay up.

[0034] Preferably, the "accelerator-preg" is coloured in an easily distinguishable manner to distinguish it from the rest of the fibrous reinforcement, unless aesthetic appearance is important where it may carry the colour (or lack of colour) of the rest of the fibrous reinforcement. In the former case, a shade of red is considered to be particularly suitable for adequately conveying the enhanced reactivity of that particular part of the assembly.

[0035] As the resin is infused into the fibrous rein-

forcement assembly and encounters the accelerator agent, the curing process is accelerated and the viscosity of the liquid resin will increase much quicker than other areas where no accelerator agent is present. Depending on the exact nature of the accelerator chosen, heat may be evolved rapidly and suitable allowance should be made for this eventuality as necessary. However, as the main application of these accelerator agents will primarily be in thin vertical sections of the fibrous reinforcement assembly where resin depletion has most tendency to occur, this reaction enthalpy should be dissipated quickly and should cause few problems. However, significant thermal conduction may also promote the cure of the non-accelerated region of adjacent resin, as described earlier, which may or may not be desirable.

[0036] The accelerator agent selected, whether for direct application to the fibrous reinforcement assembly or for pre-impregnation onto or within an "accelerator-preg", will depend on the specific resin/curing agent mixture present in the composition. For any given resin/curing agent mixture, any suitable accelerator agent could be used to initiate the localised gelation of the liquid resin. The main criteria that such accelerators should preferably meet are as follows:

- (i) to be non-volatile under vacuum;
- (ii) to mix quickly and easily with the liquid resin/curing agent mixture;
- (iii) to be compatible with the cure of the infusion resin/curing agent system;
- (iv) to be readily locatable on the fibrous reinforcement; and
- (v) to promote the rapid and efficient cure of the infusing resin system.

[0037] In some cases, it is preferable that the resin is an epoxy resin mixed with an amine curing agent and, in such cases, the accelerator may be a reagent which can react with either the amine curing agent and/or the epoxy resin to speed up or advance the cure. Typical accelerator agents that could be used to cause the localised gelation of an epoxy resin/amine curing agent mixture are inorganic salts of various metals. Suitable examples of such salts include those described in US 4,668,736, US 5,198,146, US 5,958,593, US 4,101,459 and US 5,442,035, the entire contents of which are incorporated herein by reference. These are known accelerators for the amine cure of epoxy resins.

[0038] Mercaptan compounds, such as those of the Capcure® range, could also be used as accelerators. Mercaptan compounds react with and cure epoxy resins very quickly, especially in the presence of tertiary amine curing agents.

[0039] The accelerator may also be an agent that un-

dergoes a Michael addition reaction with the amine curing agent to form an adduct, which then goes on to react with the epoxy resin to form a highly cross-linked resin matrix. One such accelerator is dipentaerythritol pentaacrylate (Sartomer® 399). Sartomer® 399 is primarily indicated for acrylate polymerisation via the 5-unsaturated residues on the molecule. Its ability to undergo a Michael addition reaction with amine curing agents has also been reported. The reaction between Sartomer® 399 and the resin/amine curing agent mixture results initially in the formation of a rubbery gel. In this form the epoxy resin is effectively immobile in the reinforcement, but retains the potential to undergo an amine cure, either by further reaction in a similar vein, or by the cure mechanism designed for the bulk of the resin infusion.

[0040] A disadvantage associated with the use of Sartomer® 399 is its potential to undergo an uncontrollable free-radical polymerisation reaction. To reduce the chance of this occurring, inhibitors can be included in the composition. As the Michael addition reaction involving Sartomer® 399 utilised in the present invention does not rely on such free-radical chemistry, the activity and loading of the free-radical inhibitors could be bolstered to further eliminate the risk of the free-radical polymerisation reaction occurring, thereby increasing the practicality and safety of this method.

[0041] The occurrence of resin depletion observed with the liquid epoxy resins is not as much of a problem with free-radically cured resin systems, such as the unsaturated polyester resins, because, unlike the epoxy resins, these resin systems can be easily modified to gel at a predetermined time following infusion. This allows the gelation to occur rapidly around the time at which the resin infusion is completed and prior to promoting the full thermal cure. This requires the judicious selection of initiators, retarders and inhibitors, which a person skilled in the art would know how to do. However, there may still be instances where the controllable, localised gelation of a free-radically cured resin may still be required. An example of such an instance would be the aforementioned application where the localised gelation of the liquid resin could be used to close off the suction applied by vacuum once the assembly or a region thereof has become fully infused with resin.

[0042] The gelation of free-radical resin systems is thermally mediated in the main and hence, could be initiated by localised heating of the composition. Additional components such as inhibitors are usually included in the composition to modify the reaction profile and to delay gelation of the resin by reacting preferentially with the initiating species. Only when these inhibitors are exhausted can the rapid polymerisation reaction really 'take hold' and the addition polymerisation reaction then promotes rapid resin gelation. Suitable combinations of components to achieve this effect are well known to those skilled in the art.

[0043] The rapid production of initiating species may also be produced in other ways, other than thermally. In

certain embodiments of the invention, the formation of highly reactive radical species could be readily promoted via the use of catalysts. These can either act as true catalysts, very small proportions functioning well even in the solid phase, or as part of a reduction-oxidation (redox) couple. Certain embodiments of the invention could involve the location of one half of a redox couple on an "accelerator-preg" and the other half in the resin/curing agent mixture. As the polyester resin is infused into the assembly, the interaction between the two halves of the redox couple could begin the rapid cure of the unsaturated species present. This reaction will be enough to overcome, at least locally, the effects of the inhibitors in the formulation. Certain metal ions could also be used to catalyse the breakdown of free radical initiators and low concentrations of suitable metal salts could be isolated on the "accelerator-pregs", or, alternatively, applied directly onto or within the fibrous reinforcement itself. It is predicted that the free radical initiators undergoing catalysed fragmentation would also function under thermal initiation, only under thermal initiation the reaction will proceed at a much more controllable rate. In essence, the object is to promote a degree of 'uncontrolled', reaction at the "accelerator-preg" site. Any of these approaches for localised catalytic initiation of polymerisation could act independently of the main reaction chemistry.

[0044] The accelerator agent, whether applied neat onto the fibrous reinforcement assembly or positioned within the assembly in the form of a pre-impregnated "accelerator-preg", can be easily applied to selected areas of the assembly where the localised immobilisation of the infused liquid resin is required. It will be appreciated that the selective positioning of the accelerator agent will dictate the pattern of pre-cure gelation that results. The pattern of gelation required will depend on each specific application. For example, in some cases, it may be advantageous to engineer the pre-cure gelation pattern so that free channels of non-immobilised resin remain through which residual air or volatile by-products may be removed from the system. This decreases the likelihood of entrapping gaseous species that would contribute to laminate porosity and cause a consequential decrease in the quality of the final structure or component.

[0045] In some cases, it will also be advantageous to leave channels of non-immobilised liquid resin within the assembly to enable the liquid resin to flow past the gelled resin, and/or over the top of it. With such an arrangement it will be more difficult for the liquid resin to flow back through the composition once the infusion is complete so this liquid resin should be retained within the desired area of the composition and thus, can be allowed to cure in the normal manner.

[0046] Furthermore, the accelerator agent may also be applied to the fibrous reinforcement in the form of one or more lines of accelerator agent applied directly onto the fibrous reinforcement, or as one or more strips

of a pre-impregnated "accelerator-preg" applied to the assembly, so that when the liquid resin comes into the accelerator agent a reaction between the accelerator and the resin/curing agent mixture will occur and result in the formation of a barrier of gelled resin which may be configured to prevent, or at least impede, the flow of the adjacent regions of liquid resin out of a selected area of the assembly. With this arrangement, the barrier effectively 'grows' from the liquid resin as the reaction with the accelerator takes place.

[0047] Alternatively, particular shapes of "accelerator-preg" patch could be used to encourage the formation of gelled or cured resin "pockets" throughout the assembly, which could be used to effectively trap and thus, prevent resin flowing out of a selected area under the effect gravity.

[0048] Preferably, following the infusion and final cure of the resin, the final composite component or structure should be indistinguishable from one that has been prepared with no local acceleration, other than the evidently improved quality in the areas prone to resin depletion where the liquid resin has been immobilised within the assembly.

[0049] The amount of accelerator applied to the fibrous reinforcement either directly or pre-impregnated within an "accelerator-preg" must be sufficient to impart the localised immobilisation of the liquid resin in the assembly. In some cases the loading required may be high (>10% by mass) and, where this is the case, the accelerator agent will work best where the resin flow rate within the assembly is low. In areas where the flow rate is high, the accelerator is likely to be washed through the assembly and diluted by the resin, as previously discussed. This may reduce the resultant increase in viscosity of the liquid resin that occurs, as well as reducing the localisation of the resin immobilisation. To allow for this occurrence, different loadings of an accelerator agent could be applied to different regions of the assembly to account for different flow rates, or, alternatively, patches of "accelerator-preg" having different loadings of the accelerator agent could be prepared for immobilising the liquid resin at different flow rates. For example, an "accelerator-preg" patch or strip could contain a high loading of accelerator for fast resin flow areas, and a lower loading for slow resin flow areas of the composition. Alternatively, a more reactive accelerator could be placed in areas where the flow of resin is fast and a lower reactivity accelerator could be applied to areas where the resin flow is slow.

[0050] An advantage of imparting the localised immobilisation of the liquid resin by causing the resin to gel by reaction with an accelerator is that during the cure cycle in which the resin composition is initially heated, the viscosity of the gelled regions of the resin remains high, thereby preventing, or at least significantly reducing, the flow of resin out of the gelled regions. This feature is particularly important if the liquid resin infused into the assembly is an epoxy resin, where an initial re-

duction in viscosity can occur during the heating of the resin for cure and the subsequent increase in viscosity as the cure takes place is usually much slower than the 'pseudo command-cure' that is possible with free radical systems. In the absence of any accelerator, the decrease in viscosity caused by the increase in temperature will, at least for a while, overcome any increase in viscosity as a result of resin advancement and continuing cure. It is during this part of the process that the problems of undesirable resin flow (as this invention is designed to protect against) will be most acute. Usually, insulating materials are used to cover the infused assembly during cure and, if this is the case, the occurrence of resin depletion may only then be apparent on demoulding the final cured component or structure. The problem is also exacerbated by the use of a low viscosity resin system, which is favoured by a number of processors of speed infusion systems.

[0051] It should also be appreciated that it is common for processors using a vacuum resin infusion process to moderate the level of vacuum applied to the assembly to suit each stage of the manufacturing process. Thus, a hard vacuum will be employed as resin is initially drawn into the reinforcement, and a softer vacuum will be used when the assembly is fully filled. The maintenance of a lower level of vacuum is important during cure to prevent the occurrence of porosity in the laminate arising from volatile matrix components, dissolved air being liberated, or volatile reaction products. Also, the continued application of at least some vacuum assists with consolidation of the structure and achievement of the correct resin/reinforcement ratio. As a consequence of the maintenance of the vacuum, the flow of any low viscosity resin within the assembly is further exacerbated.

[0052] Moreover, it is often found difficult to produce a uniform heating distribution on large moulds, such as, for example, a wind turbine blade mould. This can result in extended cure times being required whilst areas that are difficult to heat are allowed to reach the required temperature. Hence a further advantage of the immobilisation of the resin by gelation in such circumstances is that it would effectively give these areas a head start, although it does not replace the requirement for thermal post curing entirely. Therefore, the judicious placement of such immobilisation means may also obviate the requirement to supply significant additional heating during the cure cycle.

[0053] In a further alternative embodiment of the invention, the chemical immobilisation means by which the viscosity of the liquid resin is increased comprises the addition of a viscosity-enhancing material in the form of extra resin which serves to increase the local viscosity of the liquid resin that infuses into a selected area. The extra resin is preferably of higher viscosity than the bulk resin and may be partially cross-linked (B-staged) or an alternative form of resin such as, for example, solid or semi-solid form of resin (for example, solid or semi-solid

bisphenol A where the infusing resin is a liquid bisphenol A or other low viscosity epoxy analogue or formulation). In most cases the additional resin will be of higher molecular weight and hence, of higher viscosity than the liquid resin used to impregnate the bulk of fibrous reinforcement. The additional resin could be applied to the fibrous reinforcement either as a paste or as neat application. In addition, the resin may also be applied directly onto the fibrous reinforcement assembly or be impregnated onto or into one or more additional sheets of a carrier substrate (e.g. sections of fabric or fibrous reinforcement) which may then be positioned on or within the fibrous reinforcement assembly. Although there are disadvantages in that the viscosity-enhancing effects may be too localised (i.e. limited to the interlaminar layers of the fibrous reinforcement only), wash out of the additional resin may occur as the liquid resin/curing agent mixture infuses through the fibrous reinforcement, and the cure may be affected by dilution of the curing agent in the liquid resin/curing agent mixture, this form of immobilisation means will be of value in certain applications.

[0054] Alternatively, the chemical means for increasing the viscosity of the liquid resin comprises the addition of a thickener or a thixotropic material. Suitable examples of thixotropic materials include hydrophobic silica (e.g. Cabosil®), zeolites, clays, short glass fibres, or beads. Such materials can be applied to the assembly dry or as a paste, although care is needed to ensure that efficient mixing occurs with the infusing resin.

[0055] In a final alternative embodiment of the present invention, the immobilisation means is a non-reactive physical barrier which is placed at a location where the flow of resin from a particular area, for example under the force of gravity, can be prevented. The barrier may be placed on the surface of the fibrous reinforcement or, where the fibrous reinforcement is composed of numerous sheets, in between those sheets to prevent resin flowing in the 'interlaminar' spaces. However, as a proportion of the resin flow also occurs through the fibrous reinforcement, the barrier should preferably also extend through the fibrous reinforcement. This may cause discontinuity in the assembly and the formation of potentially undesirable resin/barrier interfaces and hence may not be suitable for all applications. In addition, in a vacuum resin infusion process, the presence of a permanent barrier is likely to impede the initial flow of the infusing liquid resin and hence, some areas may be slow to infuse, or may be staved of resin permanently.

[0056] The liquid resin may impregnate or infuse into the fibrous reinforcement assembly by any suitable resin infusion or impregnation process. Preferably, the resin is infused by a liquid resin infusion process such as, for example, a VARTM, SCRIMP, RIFT or RTM process.

[0057] In the compositions and process of the present invention, the fibrous reinforcement assembly may be made from any of the materials mentioned above as possible carrier substrates of the "accelerator-preg" as-

sembly.

[0058] The selection of the appropriate curing agent to be mixed with the resin will depend on the type of resin used and a person skilled in the art would readily appreciate how to select appropriate combinations.

[0059] For the purpose of illustration only, an embodiment of the invention is described in further detail below in reference to the accompanying drawing.

[0060] Figure 1 is a diagrammatic illustration of the end portion of a resin infusion lay-up assembly for a large structural component, in partial section.

[0061] The end portion of the vacuum resin infusion lay-up assembly 101 shown in Figure 1 includes a mould 102 for a large structural component, which in this case is a wind turbine blade. In contact with the surface 102a of the mould 102 is a fibrous reinforcement assembly 103, which is covered with an impervious outer sheet 104 to form a sealed vacuum bag.

[0062] The fibrous reinforcement assembly 103 consists of several sheets of reinforcing fabric fixed together. In the main body of the lay-up assembly, i.e. the region represented by arrow 107 in Figure 1, a SCRIMP-style infusion net is positioned between the fibrous reinforcement 103 and the impervious outer sheet 104.

[0063] The vacuum bag is connected to a vacuum pump (not shown), the operation of which results in the evacuation of the vacuum bag (and hence, the fibrous reinforcement 103 encapsulated therein) and causes a liquid resin/curing agent mixture, such as, for example, Prime 20 from SP Systems Ltd. (which is a two-part liquid resin and curative system in which the two ingredients are pre-mixed in the correct ratio just prior to injection/infusion), to be drawn into the fibrous reinforcement assembly 103 from a supply drum (not shown) through the resin inlet tube 105. Resin infusion channels (not shown) are provided to enable the resin to permeate through the fibrous reinforcement assembly 103 in a controlled manner. The lay-up assembly shown in Figure 1 is designed so that resin flows rapidly across the main body region represented by arrow 107 and then permeates more slowly towards the mould surface 102a. The flow into the vertically inclined sections of the lay-up assembly, such as region 106 shown in Figure 1, then occurs in the direction of arrow 108.

[0064] Once fully infused with the liquid resin/curing agent mixture, the resin is then cured to form the wind turbine blade section.

[0065] As previously discussed, it has been observed that the liquid resin/curing agent mixture infused into the assembly tends to flow out of certain areas of the assembly before the cure of the resin can be facilitated. The most notable areas where this phenomenon has been observed to occur are the areas surrounding the vacuum suction tubing, which connects the vacuum pump to the assembly, and the areas of the assembly that are in contact with vertically inclined sections of the mould surface, such as the region 106 in Figure 1. Region 106 corresponds to the glue flange of the wind tur-

bine blade and the occurrence of resin depletion in this part of the blade structure can be particularly detrimental to the mechanical properties and performance of this flange.

[0066] Therefore, to prevent liquid resin/curing agent mixture from flowing out of this region of the lay-up assembly, "accelerator-preg" patches 110a, 110b and 110c are positioned on and/or within the fibrous reinforcement 103 (as shown in Figure 1) prior to the infusion of the liquid resin/curing agent mixture. These patches are composed of one or more sheets of fabric (or any other suitable fibrous carrier material) that are impregnated with an accelerator substance which is capable of reacting with the liquid resin/curing agent mixture to impart its localised gelation, as hereinbefore defined.

[0067] As the liquid resin/curing agent mixture infuses into the vertically inclined region 106 of the fibrous reinforcement assembly 102, it comes into contact with the accelerator substance and the gelation reaction then occurs. This gelation reaction increases the viscosity of the liquid resin/curing agent mixture in the vicinity of the "accelerator-preg" patch, which in turn prevents, or at least minimises, the occurrence of resin depletion from this region due to the effect of gravity. The resin can then be cured in the normal manner to form a wind turbine blade having a substantially uniform distribution of resin throughout its entire structure, including the glue flange.

Claims

1. A fibrous reinforcement assembly with a mixture of a liquid resin and a curing agent for the resin, wherein said fibrous reinforcement assembly further comprises immobilisation means disposed at one or more locations on and/or within the fibrous reinforcement, said immobilisation means being configured to impart the localised immobilisation of the liquid resin in the vicinity of the immobilisation means.
2. An assembly according to claim 1, wherein the assembly comprises a plurality of sheets or plies of the fibrous reinforcement material.
3. An assembly according to claim 1 or claim 2, wherein the immobilisation means is a physico chemical means or a physical barrier.
4. An assembly according to claim 3, wherein the physico chemical means comprises an accelerator agent or additional resin of higher viscosity than the liquid resin.
5. An assembly according to claim 4, wherein the accelerator agent is applied onto and/or impregnated within the fibrous reinforcement assembly.
6. An assembly according to claims 1, wherein the liquid resin reacts with the accelerator agent to form a gel.
7. An assembly according to any preceding claim, wherein additional components are included with the accelerator agent for modifying the physical properties thereof.
8. An assembly according to claim 7, wherein additional components are selected from thickeners and thixotropic materials.
9. An assembly according to claim 8, wherein the thixotropic material is selected from hydrophobic silica, zeolites, clays, short glass fibres or beads.
10. An assembly according to any preceding claim, wherein the resin is an epoxy resin mixed with an amine curing agent.
11. An assembly according to any of claims 1 to 9, wherein the resin is an unsaturated polyester resin.
12. An assembly according to any preceding claim, wherein the localised immobilisation of the liquid resin defines one or more channels.
13. An accelerator-preg for placement on and/or within a fibrous reinforcement assembly comprising a carrier substrate impregnated with an accelerator agent.
14. An accelerator-preg according to claim 13, wherein the carrier substrate comprises natural or synthetic textile material.
15. An accelerator-preg according to claim 13 or claim 14, wherein the carrier substrate is impregnated with neat accelerator.
16. An accelerator-preg according to any of claims 13 to 15, wherein the accelerator agent is applied to the substrate in the form of a solvent solution.
17. An accelerator-preg according to any of claims 13 to 16, wherein the carrier substrate is secured to a fibrous reinforcement assembly by way of a glass fibre stitch or knot.
18. An accelerator-preg according to any of claims 13 to 17, wherein the accelerator-preg is coloured.
19. A process for the preparation of a fibre-reinforced composite structure or component comprising the steps of:
 - i) placing a fibrous reinforcement assembly in

a mould for said structure or component;

ii) infusing said fibrous reinforcement assembly with a mixture of a liquid resin and a curing agent for said liquid resin; and

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iii) facilitating the cure of said liquid resin;

wherein immobilisation means is disposed at one or more locations on and/or within the fibrous reinforcement, said immobilisation means being configured to impart the localised immobilisation of the liquid resin the vicinity of the immobilisation means.

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20. A process according to claim 19, wherein the immobilisation means is a physicochemical and/or physical barrier.

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21. A process according to claim 19 or claim 20, wherein the immobilisation means is an accelerator agent.

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22. A process according to claim 21, wherein the accelerator agent is applied to the fibrous reinforcement material as a neat accelerator, a solvent solution or an accelerator-preg.

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23. A process according to any of claims 19 to 22, wherein a vacuum is applied to the assembly to draw resin into the assembly.

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24. A process according to claim 23, wherein the vacuum is reduced, thus the assembly is filled with resin.

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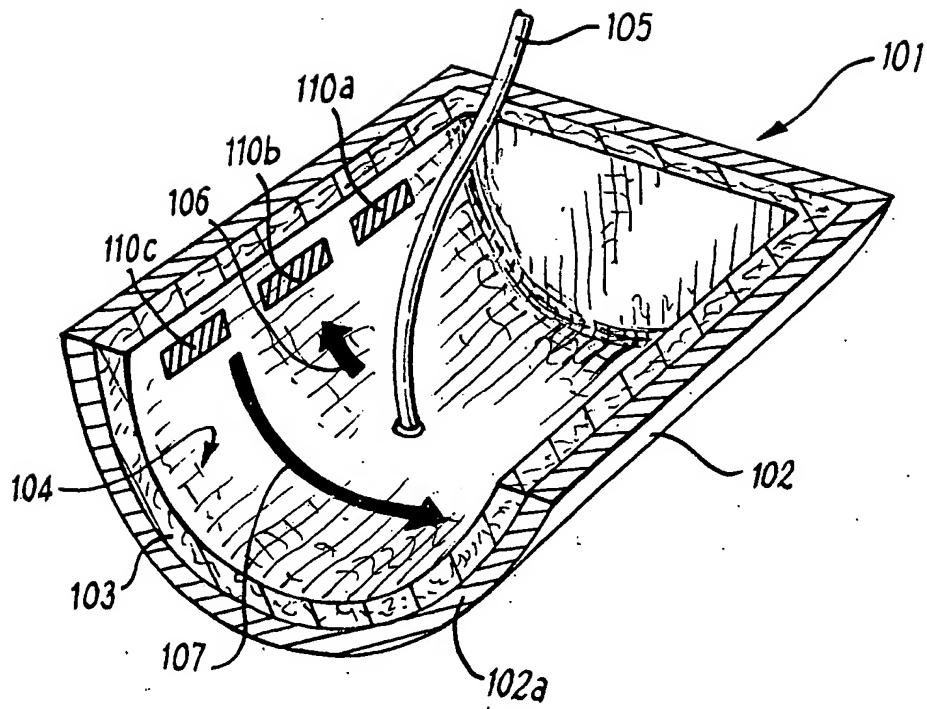


FIG. 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 25 7722

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	<p>PFUND B: "RESIN INFUSION IN THE US MARINE INDUSTRY"</p> <p>REINFORCED PLASTICS, ELSEVIER ADVANCED TECHNOLOGY, NEW YORK, NY, US,</p> <p>vol. 38, no. 12,</p> <p>1 December 1994 (1994-12-01), pages 32-34, XP000478251</p> <p>ISSN: 0034-3617</p> <p>* page 33, column 1, paragraph 4 *</p>	<p>1-4, 10,</p> <p>11, 19,</p> <p>20, 23, 24</p>	<p>B29C70/54</p> <p>B29C35/02</p>
			<p>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</p>
			<p>B29C</p>
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		14 April 2004	Van Wallene, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

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